

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant(s) : CHOY and BAI  
Serial No. : To Be Assigned  
For : FILM COATING DEPOSITION AND POWDER  
FORMATION  
Filed : Concurrently Herewith  
Examiner : To Be Assigned  
Art Unit : To Be Assigned

745 Fifth Avenue  
New York, NY 10151

**EXPRESS MAIL**

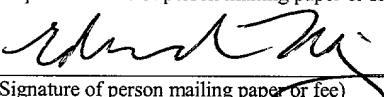
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Edward Nay

(Typed or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

**PRELIMINARY AMENDMENT**

Commissioner for Patents  
Washington, D.C. 20231  
Box Application

Dear Sir:

Prior to examination and fee calculation, please amend the application, without prejudice, without admission, without surrender of subject matter, and without any intention of creating any estoppel as follows:

100456-2003.1

**IN THE SPECIFICATION:**

Please amend the specification, without prejudice, without admission, without surrender of subject matter, and without any intention of creating any estoppel as follows:

Page 1, below "FILM OR COATING DEPOSITION AND POWDER FORMATION" please insert:

**--RELATED APPLICATIONS**

This application is a continuation of U.S. application Serial No. 09/091,456, filed June 15, 1998 which is the national phase application of PCT/GB96/03105 filed December 16, 1996, and claims priority from Great Britain applications 9525505.5, filed December 14, 1995, 9617243.1 filed August 16, 1996, and 9619146.5, filed September 13, 1996.

**FIELD OF THE INVENTION--.**

Page 1, after paragraph 2, and before paragraph 3 (after "example, structural... applications." and before "As background,..."), please insert:

**--BACKGROUND--.**

Page 1, fourth paragraph, please amend to read as follows:

The following are examples of previously proposed techniques for generating such films, coatings and powders: physical vapour deposition (PVD) (a generic term given to a variety of sputtering techniques such as radio frequency (RF) sputtering, reactive magnetron sputtering and ion beam sputtering); flame spray deposition (FSD); the so-called sol-gel process; electrostatic spray pyrolysis (ESP); and chemical vapour deposition (CVD). Two such examples are disclosed in EP-A-0 103 505 and Applied Physics Letters, Vol. 67, No. 22, Nov. 1995, pp 3337-3339.

Page 1, fifth paragraph, please amend to read as follows:

However, none of these techniques has been found to provide good control of the stoichiometry, morphology, microstructure and electrical properties of multicomponent oxide films and a relatively high growth rate and deposited area of a deposited film. Also the CVD and PVD techniques tend to need expensive equipment and highly skilled technicians for effective operation.

Page 1, after paragraph 5, and before paragraph 6, (after "skilled technicians...operation." and before "This invention provides a method of depositing...") please insert:

--SUMMARY OF THE INVENTION--.

Page 1, sixth paragraph, please amend to read as follows:

This invention provides a method of depositing a material onto a substrate, the method comprising the steps of:

feeding a material solution comprising one or more precursor compounds, a solvent and a pH-modifying catalyst to an outlet to provide a stream of droplets of the material solution;  
generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and  
providing an increase in temperature between the outlet and the substrate.

Page 1, seventh paragraph, beginning at page 1, line 31, spanning to page 2, line 7, please amend to read as follows:

This invention also provides apparatus for depositing films on a substrate, the apparatus comprising:

an outlet for providing a stream of material solution droplets, the material solution comprising one or more precursor compounds, a solvent and a pH-modifying catalyst;  
means for generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and

a heater for heating the substrate and providing an increase in temperature between the outlet and the substrate.

Page 3, after paragraph 8, and before paragraph 9 (after “The apparatus may also comprise...said coating solution.” and before “The invention will now be described...”), please insert:

--BRIEF DESCRIPTION OF THE DRAWINGS--.

Page 4, eighth paragraph, please amend to read as follows:

Figure 12 (curves A and B) show x-ray diffraction patterns for the nano-powders produced at 500° C and 800° C respectively; and

Page 4, after paragraph 9 and before paragraph 10 (after “Figure 13 and 14...” and before “In a first embodiment...”), please insert:

--DETAILED DESCRIPTION--.

Page 9, last paragraph, continuing onto page 10, please amend to read as follows:

Referring back to Figure 1, because the temperature gradient generated by the projections of the substrate holder 4 towards the outlet 5 is not necessarily constant in front of the substrate 14 in the plane of the substrate, the uniformity of coating thickness can be improved by rotating and/or translating (in general, moving) the outlet and/or the substrate holder during deposition to vary the relative positions of the outlet and the substrate with time. If rotary motion is used, this could involve, for example, rotating the substrate (which might be three-dimensional) about an axis passing through the substrate, or possibly rotating the outlet (or outlets, if more than one is used) about an axis which is not coaxial with the outlet's axis (i.e. “circling” the outlet around).

Page 10, last paragraph, continuing onto page 11, please amend to read as follows:

The apparatus of Figure 4 is similar to that of Figure 1, except that a shaped substrate holder 104 projects towards the outlet 5 at either side of the substrate 14'. The substrate holder

104 is heated as before, and this heating serves to set up a temperature gradient whereby the ambient temperature increases as the substrate 14' is approached from the direction of the outlet 5. (The arrangement of Figure 1 also provided an increase in temperature approaching the substrate 14 from the direction of the outlet 5, but the arrangement of Figure 4, with the projecting parts of the substrate holder 104, provides a more gradual temperature gradient). This increased temperature and more gradual temperature gradient facilitates solvent evaporates and decomposition of the coating solution near the vicinity of the substrate that enables decomposition of the film.

Page 12, last paragraph, continuing onto page 13, please amend as follows:

In this way, the electrostatic field set up between the charged outlet 5 and substrate holder 104 serves to guide charged coating solution droplets to the substrate 14'. As described earlier, droplets of the coating solution are provided with a negative charge by way of the high voltage DC source 1. These negatively charged droplets are thus attracted onto the substrate and in moving towards the substrate pass through a region of increasing temperature gradient. The temperature gradient ensures that the solvent evaporates before the PVDF precursor droplets reach the substrate 14' and the chemical reaction occurs just on or in very close vicinity of the substrate surface to form a PVDF crystal phase film coating.

Page 13, sixth full paragraph, please amend to read as follows:

It is thus known that there are at least two stable crystal forms of PVDF, a T-G-T-G non-polar form ( $\alpha$ -phase) and a planar zig-zag polar form ( $\beta$ -phase). One can obtain an oriented  $\beta$ -form from the  $\alpha$ -form in PVDF films by mechanical stretching or rolling, corona discharge, and high temperature high voltage poling. A number of researchers have shown that the  $\beta$ -form is very important in obtaining good piezoelectricity and pyroelectricity in PVDF films.

Page 14, last paragraph, continuing onto page 15, please amend to read as follows:

From the results of IR analysis between process I and II, it is clear that the contents of  $\beta$ -phase is higher in the PVDF film produced using process II, but a certain amount of  $\alpha$ -phase may still exist under process II. It indicates that PVDF films prepared by process II consist mainly of the  $\beta$  crystal phase with some  $\alpha$ -phase. Meanwhile, it is also found that corona field strongly influenced the surface structure of PVDF film. From the spectra, it is observed that since the absorption peak at about  $1280\text{ cm}^{-1}$  in process II is assigned to the  $\text{CF}_2$  symmetric stretching vibration of  $\beta$  crystal phase, and is stronger than that in process I, the results of the IR spectra suggest that  $\beta$ -form crystal is oriented and the  $\text{CF}_2$  dipoles are aligned along the applied corona field.

Page 15, first full paragraph, please amend to read as follows:

There have been many investigations of  $\alpha$ -phase and  $\beta$ -phase crystal in PVDF film. It is well known that the  $\alpha$ -phase crystal is more stable than the  $\beta$ -phase crystal. The reason why the  $\beta$ -phase crystal was formed in spite of its instability was not clear. In the present case of ESAVD, it is proposed that the stability and the mechanism of  $\beta$ -phase crystal formation is as follows. Because  $\beta$ -phase crystal is the polar crystal,  $\beta$ -phase is stabilized and formed in preference to  $\alpha$ -phase when the corona field exists during the deposition of PVDF film. Consequently, the content of  $\beta$ -phase increases with increasing the energy supplied to the substrate by the corona discharge. Under the conditions shown in the experimental section, the charged droplets of the PVDF solution were attracted onto the substrate and the PVDF film was formed by evaporation of the solvent and decomposition of precursor solution during substrate temperature field. PVDF polymer seems to have enough mobility to change the conformation aligned along the applied field direction under the existence of the corona field during evaporation of the solvent. But if the corona field does not exist after deposition (as process I), a certain amount of energy is obtained to rearrange the PVDF molecules because the substrate temperature is high enough near/or over PVDF melting point  $170^\circ\text{C}$ . In contrast, when a corona field exists during cooling down of the PVDF film to room temperature, the polar groups in PVDF film are "cooled" along the applied corona field direction.

Page 15, second full paragraph, please amend to read as follows:

Figures 9a and 9b are schematic diagrams showing dipole orientation in polymer films produced by the two process variants, process I and process II. These illustrate that under process II a PVDF film with oriented  $\beta$ -phase crystal is obtained, which is very important for getting good piezoelectricity and pyroelectricity in PVDF film.

Page 15, last paragraph, continuing onto page 16, please amend to read as follows:

The present studies thus show that the oriented thin PVDF film can be prepared directly onto a substrate in a single step by a novel ESAVD technique. The corona field is maintained during substrate cooling to form oriented polar polymer film PVDF, but other forms of PVDF can be produced without maintaining the field. The corona field helps to transport the charge droplets of PVDF solution onto the substrate to form PVDF thin film, and forces the polar group in PVDF thin film to align along the corona field.

Page 16, second paragraph, please amend to read as follows:

The present results also clearly revealed the potential of this technique to deposit polymer thin film of good quality material with very simple equipment. This technique can be used in the fabrication of a wide range of polymer films, including polar and conductive polymer/or co-polymer coatings, such as PVDF, PTFE, polyanilines, and polypyrrole etc.

Page 16, third paragraph, please amend to read as follows:

Figure 10 illustrates a third embodiment of a deposition apparatus. In many respects, the apparatus of Figure 10 is similar to that of Figure 4, but for the addition of deflectors 210 under the control of a deflection controller 200 (components analogous to those in Figures 1 and 4 are similarly numbered in Figure 10, which the use in Figure 10 of a prime (') or double prime (") after the number).

Page 18, first paragraph, please amend to read as follows:

The quality of the YSZ nanopowders depends strongly on the process conditions. Below a reaction temperature of 450°C, all samples appeared to be amorphous from the x-ray diffraction traces. Figure 12 (curves A and B) shows x-ray diffraction patterns for the nano-powders produced at 500°C and 800°C respectively. The x-ray diffraction patterns show that fully stabilized cubic zirconia (YSZ) nanopowders are directly formed. The presence of monoclinic or free  $Y_2O_3$  phases was not detected in YSZ powders produced at about 500°C. No other new phases were observed. It indicates that  $Y_2O_3$  has been perfectly dissolved into the  $ZrO_2$  lattice to form a solid solution.

Page 18, second paragraph, please amend to read as follows:

Figures 13 and 14 show the microstructures of YSZ nanopowders at different reaction temperatures. In the nanopowder formation process, the YSZ aerosol is produced by electrostatic assisted spray, and delivered into the reaction zone in a CVD reactor chamber, with the fine droplets of aerosol being converted into dry gel and pyrolyzing to form the nanopowders onto cold substrate under an appropriate low temperature. TEM micrographs reveal that the distribution of YSZ nanoparticles is uniform and the average size of YSZ powders deposited at 500°C is 10-20 nm (Figure 13). Under the high reaction temperature (e.g. 800°C), particle cluster aggregation occurs. TEM micrographs reveal that the distribution of YSZ nanoparticles is not uniform, and the YSZ particle size is in the range of 30-80 nm at high temperatures (Figure 14).

**IN THE DRAWINGS:**

Please amend the drawings without prejudice, without admission, without surrender of subject matter, and without any intention of creating any estoppel as follows:

Please amend Figure 12 as shown on the enclosed red-lined version.



**REMARKS**

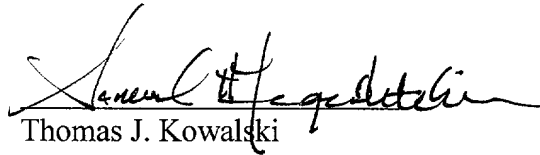
This preliminary amendment serves to accurately describe the lineage of the present application and to incorporate amendments to the specification and drawings made during the prosecution of the parent application.

No new matter is added.

Early and favorable examination on the merits is respectfully requested.

Respectfully submitted,  
FROMMER LAWRENCE & HAUG LLP

By:



Thomas J. Kowalski

Reg. No. 32,147

Samuel H. Megerditchian

Reg. No. 45,678

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

Page 1, after paragraph 5, and before paragraph 6, (after “skilled technicians...operation.” and before “This invention provides a method of depositing...”):

**RELATED APPLICATIONS**

This application is a continuation of U.S. application Serial No. 09/091,456, filed June 15, 1998 which is the national phase application of PCT/GB96/03105 filed December 16, 1996, and claims priority from Great Britain applications 9525505.5, filed December 14, 1995, 9617243.1 filed August 16, 1996, and 9619146.5, filed September 13, 1996.

**SUMMARY OF THE INVENTION**

Page 1, sixth paragraph:

This invention provides a method of depositing a material onto a substrate, the method comprising the steps of:

[(a)]feeding a material solution comprising one or more precursor compounds, a solvent and a pH-modifying catalyst to an outlet to provide a stream of droplets of the material solution[.];

[(b)]generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and

[(c)]providing an increase in temperature between the outlet and the substrate.

Page 1 seventh paragraph, beginning at page 1, line 31, spanning to page 2, line 7:

This invention also provides apparatus for depositing films on a substrate, the apparatus comprising:

[(a)]an outlet for providing a stream of material solution droplets, the material solution comprising one or more precursor compounds, a solvent and a pH-modifying catalyst;

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[(b)]means for generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and

[(c)]a heater for heating the substrate and providing an increase in temperature between the outlet and the substrate.

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BRIEF DESCRIPTION OF THE DRAWINGS

Page 4, eighth paragraph:

Figure 12 (curves A [a] and B [b]) show x-ray diffraction patterns for the nano-powders produced at 500° C and 800° C respectively; and

Page 4, after paragraph 9 and before paragraph 10 (after “Figure 13 and 14...” and before “In a first embodiment...”):

DETAILED DESCRIPTION

Page 9, last paragraph, continuing onto page 10:

Referring back to Figure 1, because the temperature gradient generated by the projections of the substrate holder [1]4 towards the outlet 5 is not necessarily constant in front of the substrate 14 in the plane of the substrate, the uniformity of coating thickness can be improved by rotating and/or translating (in general, moving) the outlet and/or the substrate holder during deposition to vary the relative positions of the outlet and the substrate with time. If rotary motion is used, this could involve, for example, rotating the substrate (which might be three-dimensional) about an axis passing through the substrate, or possibly rotating the outlet (or outlets, if more than one is used) about an axis which is not coaxial with the outlet's axis (i.e. “circling” the outlet around).

Page 10, last paragraph, continuing onto page 11:

The apparatus of Figure 4 is similar to that of Figure 1, except that a shaped substrate holder 104 projects towards the outlet 5 at either side of the substrate 14'. The substrate holder 104 is heated as before, and this heating serves to set up a temperature gradient whereby the ambient temperature increases as the substrate [106] 14' is approached from the direction of the outlet [107] 5. (The arrangement of Figure 1 also provided an increase in temperature approaching the substrate 14 from the direction of the outlet 5, but the arrangement of Figure 4, with the projecting parts of the substrate holder 104, provides a more gradual temperature gradient). This increased temperature and more gradual temperature gradient facilitates solvent evaporates and decomposition of the coating solution near the vicinity of the substrate that enables decomposition of the film.

Page 12, last paragraph, continuing onto page 13:

In this way, the electrostatic field set up between the charged outlet [107] 5 and substrate holder 104 serves to guide charged coating solution droplets to the substrate 14'. As described earlier, droplets of the coating solution are provided with a negative charge by way of the high voltage DC source 1. These negatively charged droplets are thus attracted onto the substrate and in moving towards the substrate pass through a region of increasing temperature gradient. The temperature gradient ensures that the solvent evaporates before the PVDF precursor droplets reach the substrate 14' and the chemical reaction occurs just on or in very close vicinity of the substrate surface to form a PVDF crystal phase film coating.

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corona field exists during cooling down of the PVDF film to room temperature, the polar groups in PVDF film are "cooled" along the applied corona field direction.

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Page 18, second paragraph:

Figures 13 and 14 show the microstructures of YSZ nanopowders at different reaction temperatures. In the nanopowder[s] formation process, the YSZ aerosol is produced by electrostatic assisted spray, and delivered into the reaction zone in a CVD reactor chamber, with the fine droplets of aerosol [change] being converted into dry gel and [pyrolysis] pyrolyzing to form the nanopowders onto cold substrate under an appropriate low temperature. TEM micrographs reveal that the distribution of YSZ nanoparticles is uniform and the average size of YSZ powders deposited at 500°C is 10-20 nm (Figure 13). Under the high reaction temperature (e.g. 800°C), particle cluster aggregation occurs. [This is because aerosol droplets changed into particles at high reaction temperatures.] TEM micrographs reveal[s] that the distribution of YSZ nanoparticles is not uniform, and the YSZ particle size is in the range of 30-80 [nanometres] nm at high temperatures (Figure 14).

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